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INFLUENCE OF CORE-SHELL GRAINS ON THE INTERNAL STRESS STATE AND PERMITTIVITY RESPONSE OF ZIRCONIA MODIFIED BARIUM TITANATE

by

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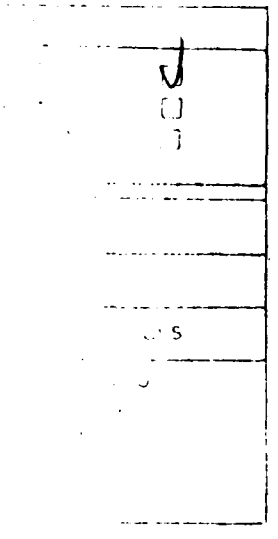

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ABSTRACT

$BaTiO_3$ modified with grain boundary resident ZrO_2 (≤2 wt%) ZrO_2 results in substantial inhomogeneities in the microstructure when sintered at 1320°C for 2h. These inhomogeneous regions were seen as core-shell grains in the microstructure and were accompanied by an increase in the internal stress level. The shells had a variable composition ($BaTi_{1-x}Zr_xO_3$) and a tetragonal structure. An expansion mismatch between the core and the shell placed the core in compression resulting in a decrease in the c lattice parameter and a pseudocubic structure. The combination of core-shell grains and increased internal stress resulted in an essentially flat permittivity response with temperature, a condition consistent with a distribution of Curie points within the ceramic.

Influence of Core-Shell Grains on the Internal Stress State
and Permittivity Response of Zirconia Modified Barium Titanate

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I. Introduction

Ceramic multilayer capacitor formulations based on $BaTiO_3$ can be chemically or physically modified to exhibit temperature-stable dielectric behavior (less than ±15% deviation), over the temperature range -55°C to 125°C. The stability can result either from chemical substitution in the ceramic, from a small-grained microstructure,[1,2] or from the presence of core-shell grains which may result from chemical inhomogeneities. Heywang,[3] described the basic structure of these latter materials as being comprised of a microstructure made up of biphasic grains (i.e. core-shell grains) as first described by Rawal.[4] This type of grain structure contains two regions, the core and the surrounding shell. The core is composed of pure barium titanate, while the shell is barium titanate modified by a cation which occupies either the A or B site in the lattice. Heywang further indicated that a microstructure composed of such core-shell grains would tend to suppress spontaneous polarization and the permittivity maxima which characterizes the ferroelectric transition. The disappearance of the transition peak, however, may also be attributed to structural changes in the $BaTiO_3$ unit cell, (i.e. formation of a pseudocubic perovskite) which can result from high internal stress in the microstructure.[2]

When $BaTiO_3$ cools through the Curie temperature, it undergoes a phase transformation from the cubic state to a tetragonal state. Accompanying this phase change is a volume expansion (≈1%) which can lead to the development of a complex stress state. The stress state exists because normal grain expansion is constrained by intergrain contacts. Some internal stress can be partially relieved by the formation of 90° twins within the

larger grains, however, the residual stresses resulting from intergrain contacts, single domain grains and core-shell configurations are not relieved by twinning. Buessem[5] suggested that the stress system may consist of a uniform compression along the *c* axis, tensile stresses along the two *a* axes or a combination to the two. These stresses would suppress the spontaneous deformation of the tetragonal unit cell forcing it to become more cubic. Buchanan and coworkers[2] have shown that this condition results from a suppression of the *c* axis, attributed to the internal stress, and as suggested by Martirena and Burfoot[6] this is a plausible explanation for the dielectric properties observed. It was, therefore, the purpose of this investigation to determine the effects of core-shell grain configurations on the internal stress state and on the structural and dielectric properties of grain boundary modified $BaTiO_3$.

II. Experimental Procedure

Samples were prepared by ball milling high purity $BaTiO_3$* (Ba/Ti=0.997) for 12h using ZrO_2 balls with 2 wt% ZrO_2**. This amount of ZrO_2 was determined to be the lowest concentration necessary to achieve a uniform microstructure.[2] Zr contamination due to ball milling was found to be less than 0.1 wt% per 150g batch. Milling was carried out in a 1.5:1 solution of isopropyl alcohol:deionized water with Menhadden fish oil*** added as a dispersant. A binder/lubricant solution composed of PVA and Carbowax 4000 was added and the slurry was milled for an additional 1.5h. The dispersed slurry was spray dried and the resulting powder uniaxially pressed into discs (16mm x 2mm, 136 MPa) and sintered at 1320°C for 2h.

Capacitance and tanδ measurements were made using an automatic capacitance bridge. Samples were deaged at 150°C for 15 min and measurements of the aging rate were carried out at 25°, 50° and 90°C up to 200h. The measurements were made

* Ticon-HPB, TAM Ceramics Inc., Niagara Falls, NY.
** Zircar Products, Inc., Florida, NY.
*** Werner G. Smith Co., Cleveland, OH.

continuously using 0.3V rms across the sample. The apparent internal stress was determined using the microindentation technique described by Okazaki.[7] The apparent stress was determined from fracture toughness and crack length data obtained from microindentations resulting from applied loads of 0.1 to 0.5 kg using a loading rate of 90 sec to avoid lateral cracking. Foils for TEM analysis were prepared by mechanical grinding samples to a thickness of 100 μm and ion beam thinning to perforation. All microscopy examinations, including convergent beam electron diffraction and selected area diffraction, were conducted on a Philips EM 420 operated at 100 kV.

III. Results and Discussion

Near theoretical densities (≈96%) were achieved when the ZrO_2 modified $BaTiO_3$ samples were sintered at 1320°C for 2h. Microstructural observation of the as-sintered surface (Fig. 1A) revealed a near uniform grain size (0.43 μm). TEM evaluation of the microstructure showed the distribution of ZrO_2 to be inhomogeneous, residing primarily at the grain boundaries.[2] Some ZrO_2 diffusion into the $BaTiO_3$ lattice could, however, be inferred from the slight down shift in the Curie peak. As shown in Fig. 1B, incorporation of the ZrO_2 into the $BaTiO_3$ at 1320°C coincided with the formation of core-shell grains in the microstructure and with liquid formation in the $BaTiO_3$ during sintering.[8] The x-ray intensity distribution (EDS) of Zr from a typical core-shell grain is shown in Figure 2. It can be seen that the relative concentration of Zr decreased as the core is approached and that no Zr is present in the core. The core-shell grains contain, therefore, a core of pure $BaTiO_3$ surrounded by a shell of Zr modified $BaTiO_3$ (i.e. $Ba(Ti_{1-x}Zr_x)O_3$).

Convergent beam electron analysis (CBED) was used to determine the structure of the Zr modified shell region. The analysis was performed with respect to the core of pure $BaTiO_3$ which has a tetragonal *4mm* point group below 120°C and orthorhombic mm2 symmetry below 5°C. The analysis was carried out with respect to the <100> beam directions which accurately distinguished between the cubic, tetragonal or orthorhombic

crystal symmetry. To determine the point group of the core and shell, examinations of the whole CBED pattern and zero order Laue zone were used to determine the diffraction group. This in turn led to the assigning of a point group after complete analysis in several beam directions.[9,10] Examination of the [100] beam direction of the core (Fig. 3A) showed that the zero layer is described by *m* symmetry. Further analysis of the whole pattern showed the *m* symmetry to be again evident. The analysis also showed that the diffraction group is m_{1r}, as expected for a *4mm* point group. Similarly, the analysis obtained from the shell region (Fig. 3B) gave identical results and therefore, both images can be described by *m* symmetry. Further analysis of the [001] electron beam direction was used to distinguish between the orthorhombic and tetragonal symmetries. Shown in Figure 4A and 4B are CBED patterns of the core and shell respectively. Both patterns can be described by *4mm* symmetry. Therefore, from the CBED analysis it was determined that the shell region is also tetragonal with a *4mm* point group symmetry.

Assuming that Zr diffuses into $BaTiO_3$ replacing Ti in the unit cell, it would be expected that the larger Zr ion would cause an increase in the unit cell dimensions and lattice parameters, as observed. The lattice parameters were estimated using selected area diffraction (SAD). The SAD patterns were analyzed for the (001) (010) and (011) planes. The resulting lattice parameters and unit cell volumes are shown in Table 1. The lattice parameters determined for the core were in close agreement with the same parameters measured in the bulk powders by x-ray diffraction. The volume expansion mismatch between the two regions was ≈4.4%. Therefore, on cooling through the ferroelectric transition the shell contracts 4.4% more than the core, placing the core in uniform compression, thereby creating a complex internal stress state in the material. The stress induced by the shell compresses the perovskite unit cell forcing it towards a cubic modification as predicted by Buessem.[5] This reduction in the *c* lattice parameter of the core is only ≈0.2% less than the *c* lattice parameter in large grained $BaTiO_3$ in which the residual stress is relieved by the high degree of twinning within grains.

The apparent internal stress was determined using a microindentation technique, shown to be applicable to ferroelectrics by Okazaki.[7] This technique allows internal stress to be determined from a plot of fracture toughness (K_{Ic}) versus the square root of the crack length. The internal stress data is given in Table 2. For constant loading during indentation a distribution of crack lengths resulted, indicating the presence of stress anisotropy within the specimen. A comparison was drawn between $BaTiO_3$ with core-shell grains in the microstructure and $BaTiO_3$ without such core-shell grains. As can be seen in Table 2, the specimen possessing the core-shell grains showed much higher internal stress after 100h of aging, compared to the similar $BaTiO_3$ without such grains in the microstructure.

Analysis in the [421] beam direction was found to be very sensitive to strain in the lattice. A higher order Laue zone (HOLZ) pattern of the core (Fig.5A) showed HOLZ deficiency lines in the central disk of the CBED pattern. The HOLZ pattern of the core region could be precisely compared to the computer simulated pattern (Fig. 5B). A similar [421] HOLZ pattern (Fig. 5C) taken in the shell, however, showed the deficiency lines to have become broad and diffuse. This indicated lattice strain in the shell region of the grain, and also the expansion mismatch between the core and shell. Extensive examination of [421] HOLZ patterns of numerous shell regions all showed broad diffuse difficiency lines indicative of lattice strain, thus ruling out contamination and specimen thickness effects on the image in Fig. 5C. The observed diffuse lines are not artifacts and, therefore, can be attributed to lattice strain as described by Steeds.[11]

The permittivity response of $BaTiO_3$ modified with 2 wt% ZrO_2 is shown in Fig. 6. The measured permittivity response was found to be relatively stable with respect to temperature and showed a suppressed ferroelectric transition region. The permittivity changed $\approx$3% over the range 30°C to 125°C and $\approx$-15% from 30°C to -55°C. The dissipation factor, tan δ, was found to decrease linearly with increasing temperature. The measured internal stress remaining in the specimen after 100h of aging was 184 MPa (1900

kg/cm^2). This amount of stress is sufficient to shift the Curie temperature by 20°C,[12,13] if it were isotropic throughout the ceramic. However, the ZrO_2 was found to be nonuniformly distributed in the matrix and the microindentation results also indicated stress variation within the specimen. This stress variation could be expected to lead to a distribution of Curie points within the specimen ranging from no shift for unmodified grains to a 20-25°C shift in the Curie temperature for the more highly stressed core-shell grains, which comprised approximately 50 vol% of the specimen. A distribution of Curie points in a bandwidth of ≈20-25°C would be sufficient to result in the observed permittivity response. The disappearance of the ferroelectric transition region in Fig. 6, therefore, can be attributed to the formation of a pseudocubic $BaTiO_3$ phase resulting from the large internal stresses induced by the core-shell grain configurations.

As shown in Table 3 the aging rate decreases with increasing aging temperature for the material containing core-shell grains. Typically, the aging rate of $BaTiO_3$ increases with temperature since the aging phenomena is a thermally activated process.[14,15] The observed decrease in aging rate, therefore, can also be attributed to the high internal stress in the ceramic. As shown in in Fig. 7 the internal stress in the specimen containing core-shell grains decreases with increasing aging temperature, however, the internal stress remaining in the ceramic is still substantially higher in these samples than in $BaTiO_3$ without core-shell grains in the microstructure. An explanation for this phenomena is that the stresses, while decreasing with increasing temperature as shown in Fig. 7, are still of sufficient magnitude to pin the domains and decrease domain wall motion, thereby decreasing the aging rate.

The overall effect of the 2 wt% ZrO_2 additions to $BaTiO_3$ specimens sintered at 1320°C for 2h, therefore, was the formation of ≈50 vol% core-shell grains in the microstructure. The shell was found to consist of Zr modified $BaTiO_3$ surrounding a core of pure $BaTiO_3$. The measured data would indicate that the higher expansion shell constrains the core, resulting in high internal stresses in the specimen, a decrease in the *c*

lattice parameter and the formation of a pseudocubic $BaTiO_3$ phase. The result of this high internal stress state is a distribution of Curie points and a flattened permittivity response with temperature.

IV. Conclusions

Zirconia additions to $BaTiO_3$ result in core-shell grains being formed in the microstructure when sintered at 1320°C for 2h. The shell was Zr modified $BaTiO_3$ possessing a tetragonal structure and a 4.4% volume difference with respect to the core. The core-shell grain configuration caused compressive stresses to be placed on the core with a resulting decrease in the *c* lattice parameter and development of a pseudocubic perovskite core structure. Associated with these changes was a suppression of the ferroelectric transition and a stabilization of the permittivity response with temperature, attributed to the formation of a distribution of Curie points in the ceramic and an averaging of the permittivity over the range of Curie temperatures. The existence of the internal stress state also resulted in a decreased aging rate as aging temperature increased.

V. Acknowledgements

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VII. List of Figures

Table 1. Lattice parameters of core, shell and bulk $BaTiO_3$ specimen with 2 wt% added ZrO_2 (1320°C/2h).

Sample	a (Å)	c (Å)	c/a	volume (Å^3)
shell	4.050 (±0.010)	4.117 (±0.004)	1.017	67.545
core	4.000 (±0.008)	4.029 (±0.010)	1.007	64.464
bulk	4.004 (±0.001)	4.027 (±0.0003)	1.006	64.560

Table 2. Apparent stress (MPa) as a function of aging time and grain size for $BaTiO_3$ modified with 2 wt% ZrO_2.

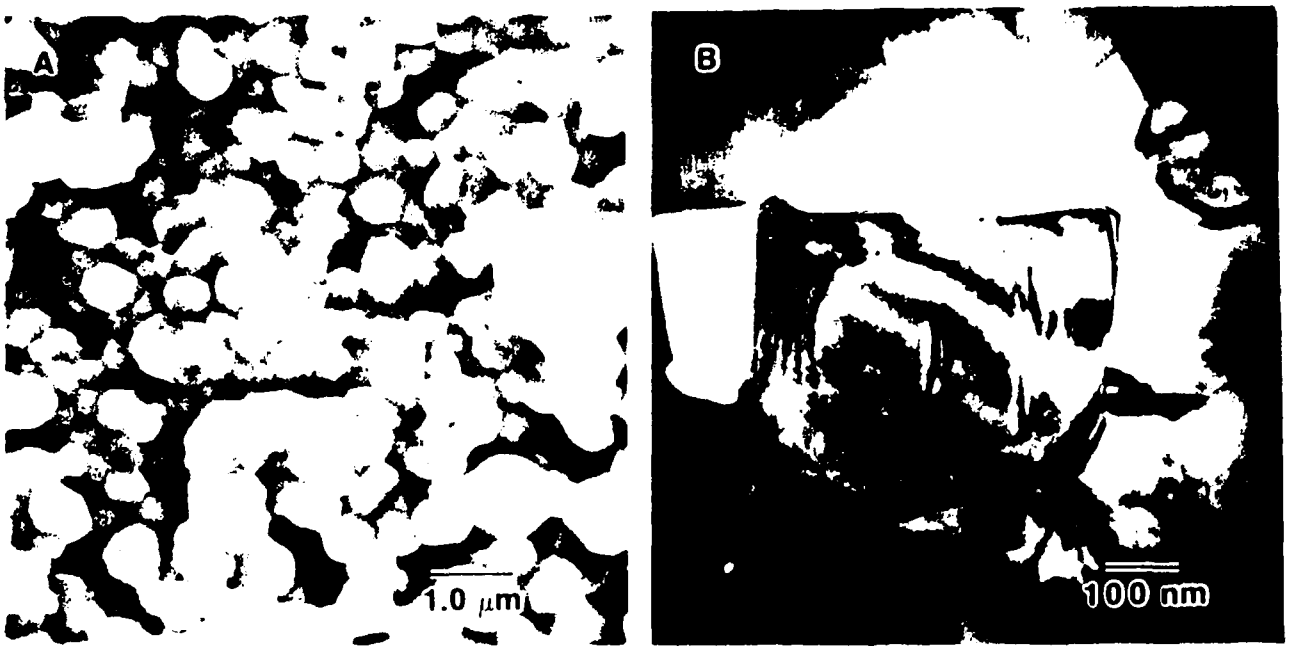
Aging Time (hr, 25°C)			Average
1	10	100	Grain Size (μm)
134	128	70	0.28
119	75	55	0.36
355	292	184	0.43*

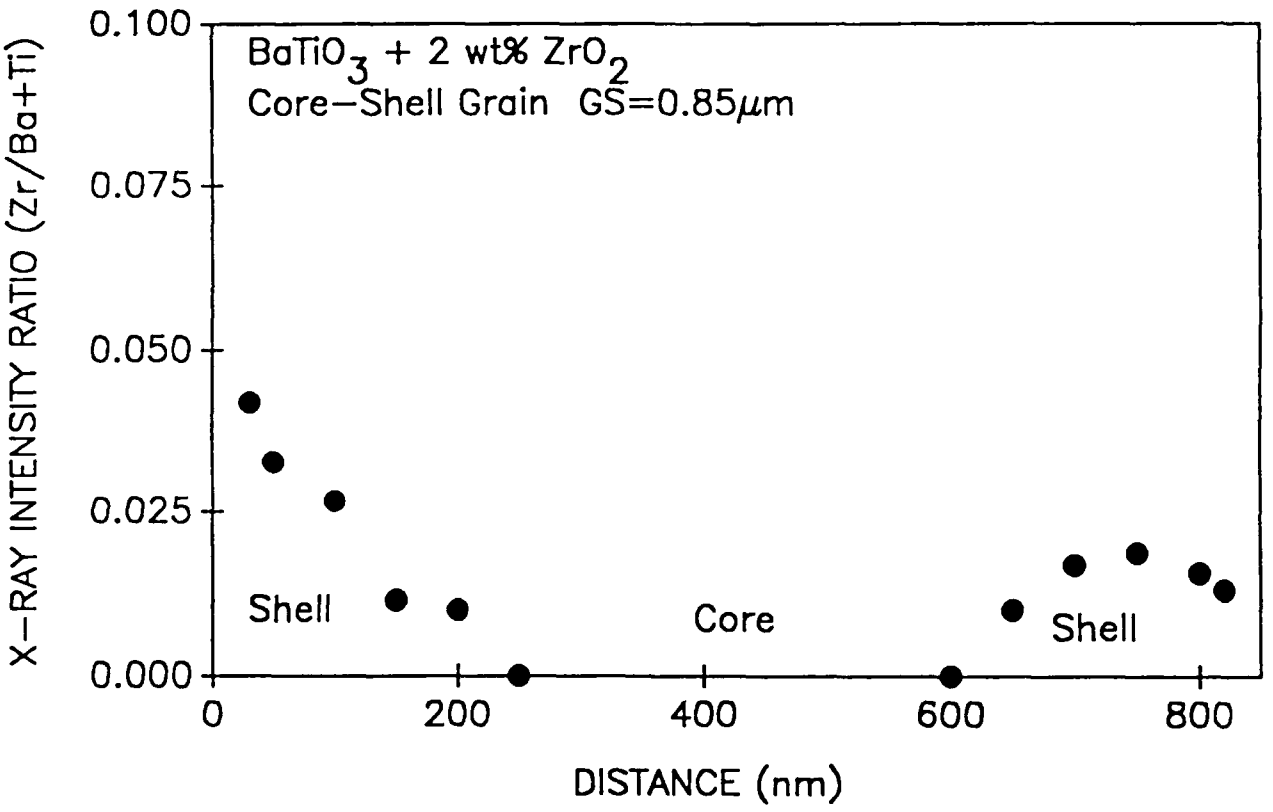
* Core-shell grains in the microstructure.

Table 3. Aging rate (%/decade) as a function of aging temperature and grain size for $BaTiO_3$ sintered with zirconia.

Sample	Average Grain Size (μm)	Aging Temperature 25°C	50°C	90°C
$BaTiO_3$				
	8.48	2.42	3.62	4.35
	9.17	2.72	3.70	4.51
	25.0	2.95	3.82	4.79
2 wt% unstabilized ZrO_2				
	0.28	1.54	1.62	1.71
	0.36	1.94	1.87	2.37
	0.43	2.54	1.07	0.85*

* Core-shell grains in the microstructure.


A
1.0 μm
B
100 nm


$BaTiO_3$ + 2 wt% ZrO_2
Core–Shell Grain GS=0.85μm
X–RAY INTENSITY RATIO (Zr/Ba+Ti)
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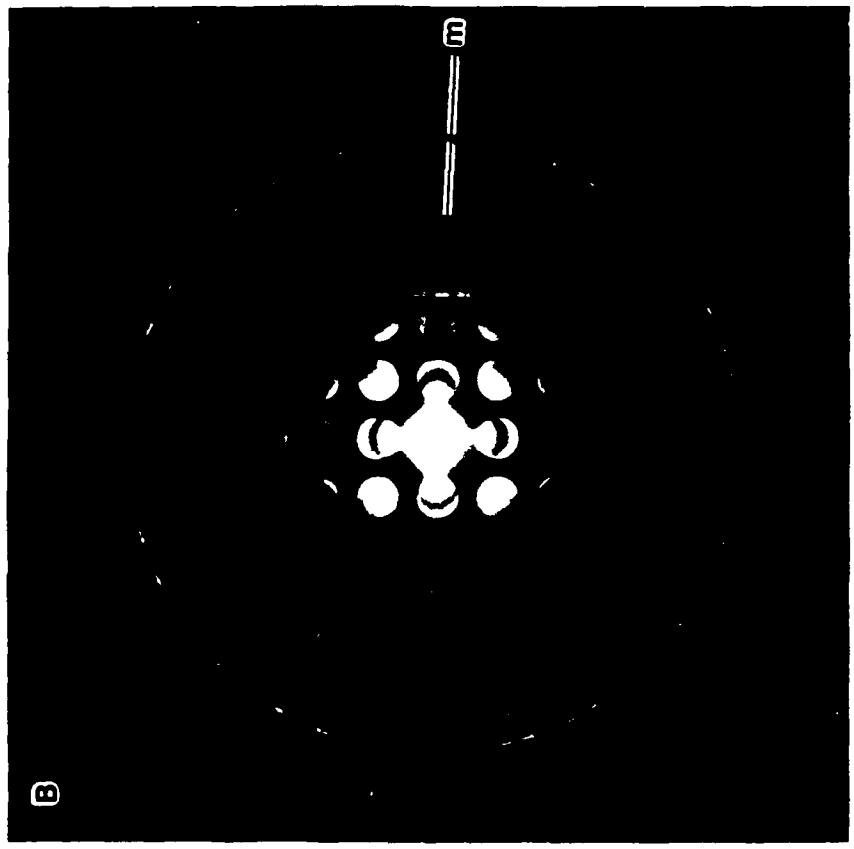
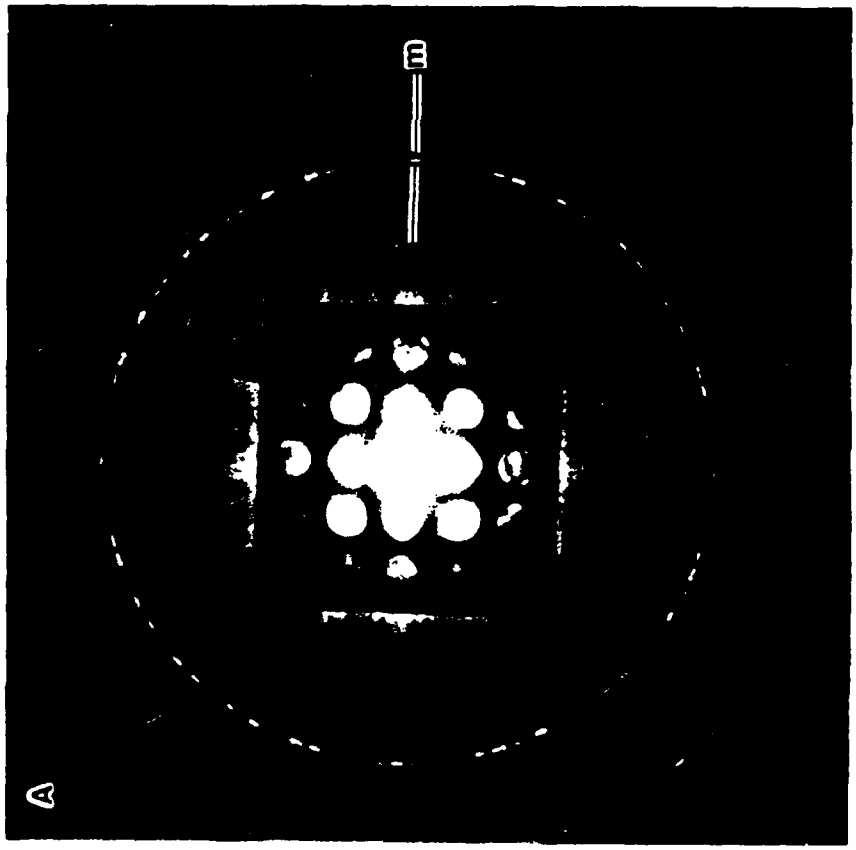
0.075
0.050
0.025
0.000
Shell
Core
Shell
0
200
400
600
800
DISTANCE (nm)


E
B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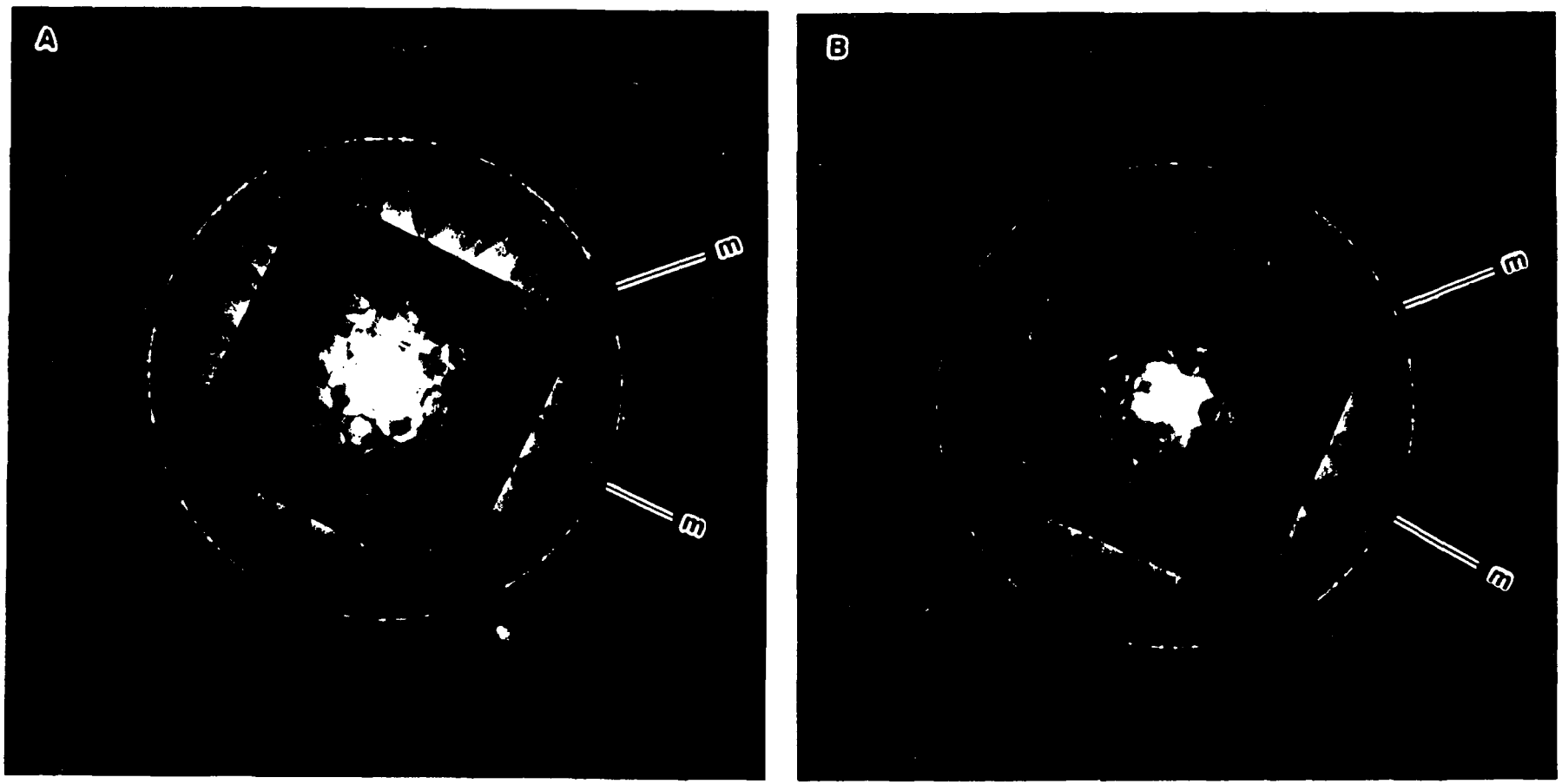
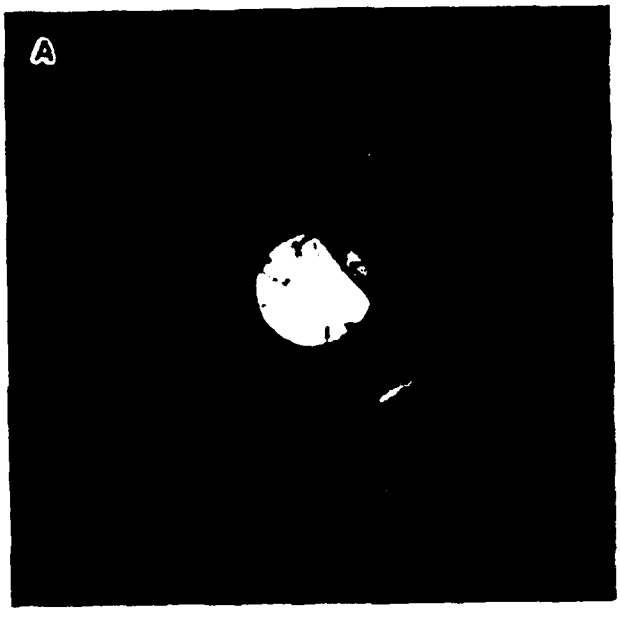
A


A
m
m
B
m
m



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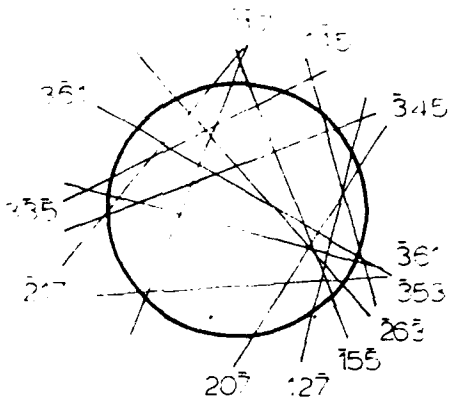
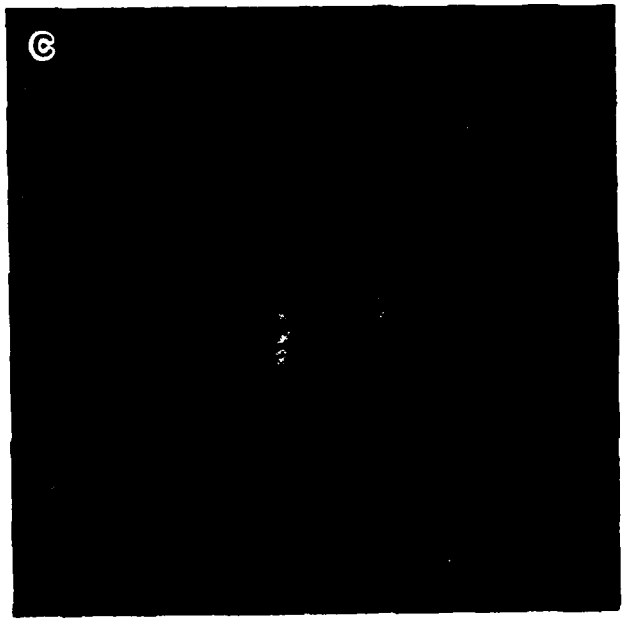
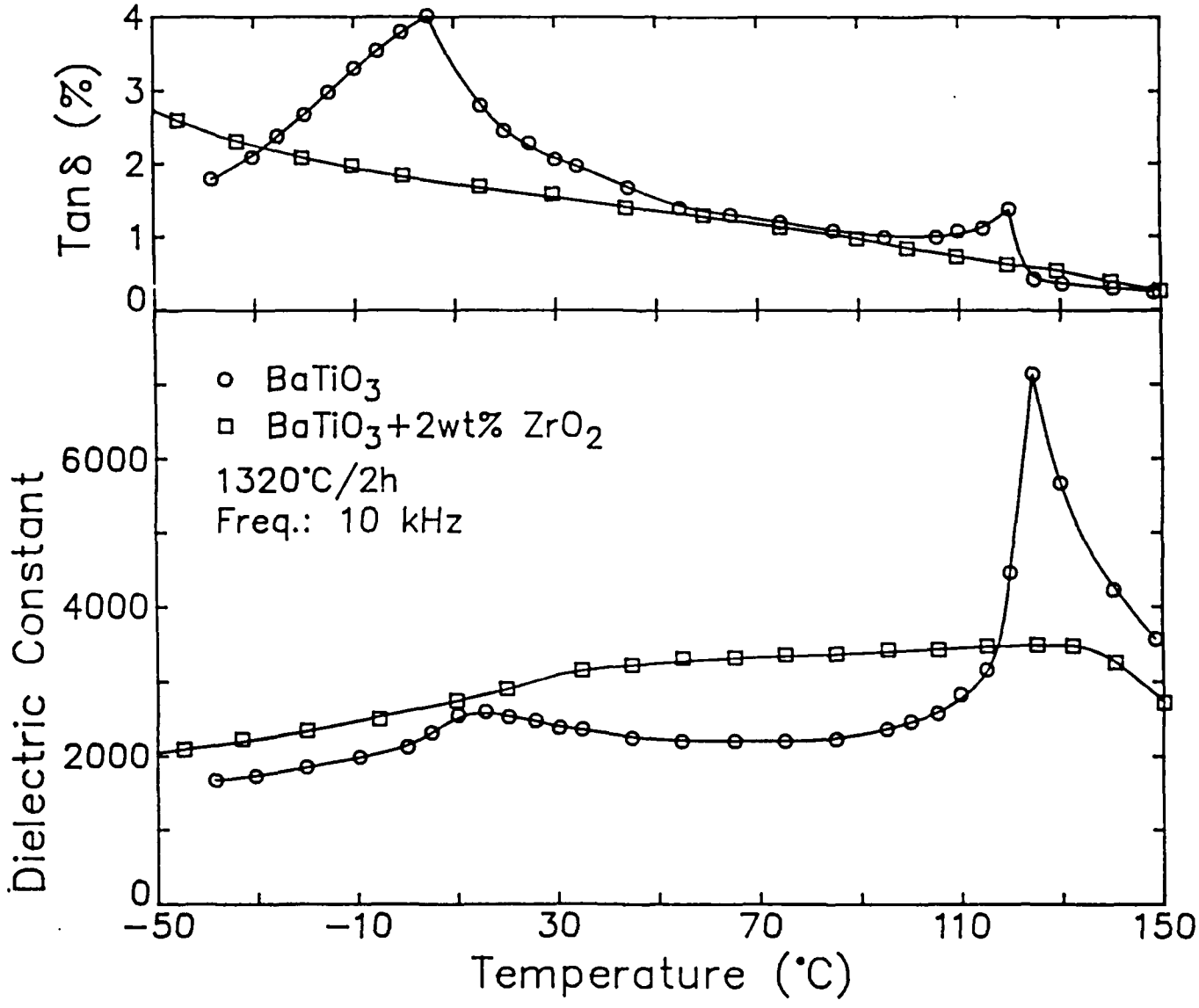
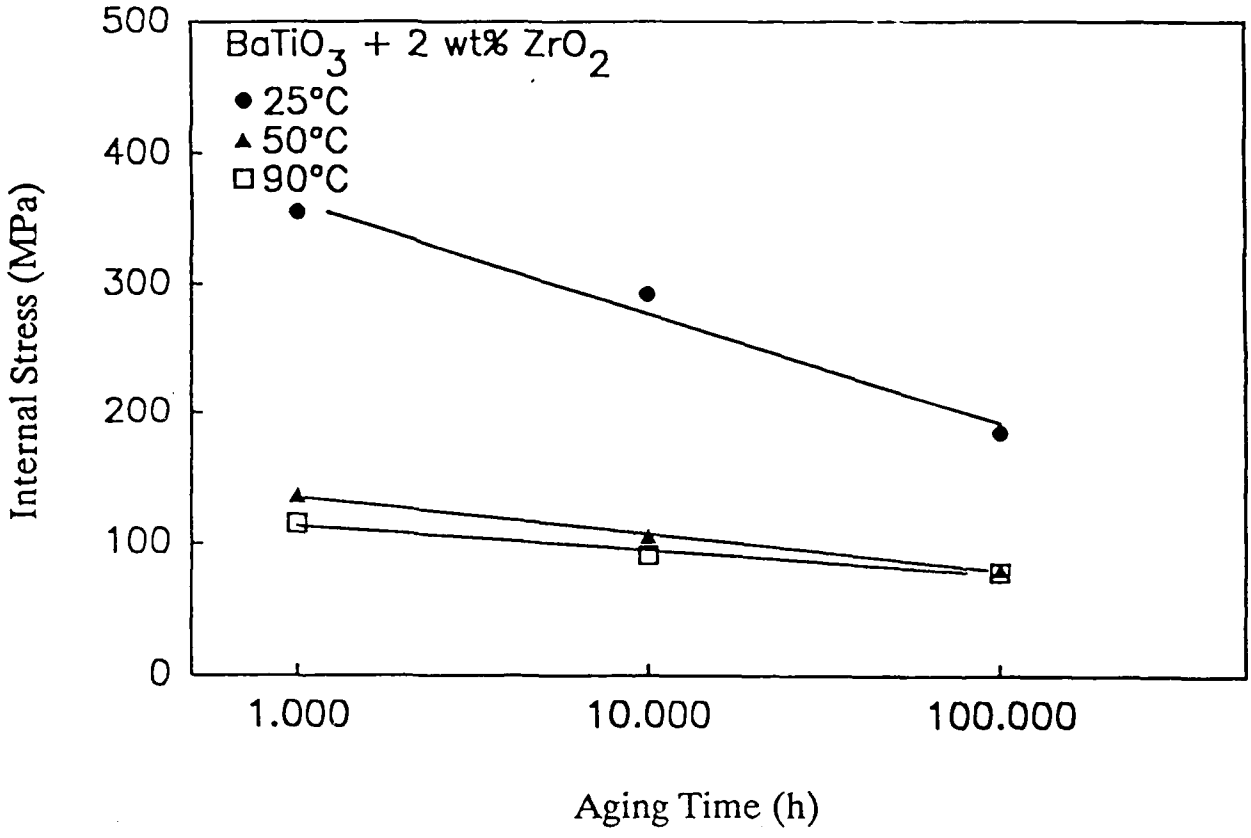





Tan δ (%)
4
3
2
1
0
BaTiO3
BaTiO3+2wt% ZrO2
1320°C/2h
Freq.: 10 kHz
Dielectric Constant
6000
4000
2000
0
−50
−10
30
70
110
150
Temperature (°C)


BaTiO3 + 2 wt% ZrO2
25°C
50°C
90°C
Internal Stress (MPa)
500
400
300
200
100
0
1.000
10.000
100.000
Aging Time (h)

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